1993 Annual Report

RESEARCH AND DEVELOPMENT

Laboratory Services Branch
Ontario Ministry of Environment & Energy

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OVERVIEW

David Boomer, Chair, R&D Committee

Since the previous Laboratory Services Branch *Annual Report on Research and Development*, the Ministry of Environment and Energy has undergone a major reorganization. The traditional Air, Water, and Waste Management branches were superceded by the *Environmental Monitoring and Reporting*, the *Program Development*, and the *Science and Technology* branches. In view of these changes, the Laboratory Services Branch also restructured to allow better delivery of services.

Irrespective of the above changes, the research and development efforts of the Laboratory Services Branch remain the same: to provide our clients with more data, faster, and at lower cost. On occasion, new methods must be developed for contaminants not previously monitored. Projects are also initiated internally that are designed to improve data quality. Because of the reorganization, the structure of this year's R&D report has been changed. Projects initiated to directly respond to the requests and concerns of our customers are described in the first section of the report. Projects principally initiated internally to improve customer service are described in the second part of the report. The principal customers for these projects (section 1), and the principal benefits of internally-initiated projects (section 2) have been specified.

As a result of projects completed last year, advances have been made in our ability to sample and detect trace elements in air. Improvements in methods for arsenic and hexavalent chromium were incorporated in our routine procedures. A project designed to investigate anomalies in polycyclic aromatic hydrocarbons (PAH) analyses resulted in new quality control protocols for storage of water samples. By using these improved procedures, degradation of PAH during sample storage was prevented. A new, more effective method for chlorophenols in sediments was also initiated after development work that employed the relatively new method of supercritical fluid extraction.

New Methods Development

Introduction

Protection of the environment is an evolving activity which requires ongoing investigations into the sources, environmental distribution, and fate of pollutants. Customers of the Laboratory Services Branch (LSB) are responsible for assessing the environmental hazards of various chemicals, and for developing guidelines and regulations to protect the environment. These guidelines may also be used for monitoring programs and site remediation activities.

LSB customers sometimes require quantitative data on the environmental concentrations of pollutants that have not previously been monitored. The LSB responds to such needs by developing new methods for these analytes, or by modifying existing methods to include additional analytes. In some cases, customer requests to lower detection limits, to improve the selectivity of methods, or to increase the applicability of methods to new sample types also require substantial modifications to methods. Most of the method development reported in this section was initiated to address the above needs.

I. Mercury Determination by ICP-MS

Study Leader:	M.Powell
Study Team:	E. Quan, D. Wiederin
Customer:	Environmental Monitoring and Reporting Branch - Drinking Water Section; Science and Technology Branch - Plant Optimization

Introduction and Objectives

Direct Injection Nebulization (DIN) is a new sample introduction system for Inductively Coupled Plasma (ICP) that increases efficiency of sample transport to the plasma. Use of this technology will result in a more efficient use of complex, expensive ICP-MS instrumentation and faster turnaround for our customers. The new methodology could save 1.5 staff-years in sample preparation time and result in improved quality control, faster sample turnaround, and lower cost.

Results

The commercial direct injection nebulizer (DIN) from Cetac Technologies has been evaluated for use with our Elan 5000 ICP-MS. A preliminary method for single element analysis of mercury has been developed.

A considerable amount of work was done in 1993 to add mercury to the current Drinking Water Surveillance Program (DWSP) scan list of 23 elements. This work involved the modification of the existing drinking water analysis method, using conventional sample introduction techniques, to the new introduction technique of DIN. The advantage of this new technique is to give the customer the option of including mercury in their analysis request without going to the conventional method of cold vapour atomic absorption.

Work to be Completed

The original feasibility study is complete for multi-element determinations. Parallel running of samples between the conventional technique and the DIN

introduction device show good comparison. Conversion of the automated sampling system has yet to be completed along with some software modification. Studies on the effects of high dissolved solids and particulate matter in samples must still be carried out with the DIN.

Although the instrumental analysis procedures for the method are near completion, field studies must be done to ensure that a proper sample preservative is used. Wall loss and leach studies must be conducted to show that nitric acid used in the new method is as efficient a preservative as the permanganate used in the existing method.

II. Chromium Speciation and Organometallic Determination by LC-DIN-ICP-MS

Study Leader: M.Powell
Study Team: D. Wiederin, Cetac Technologies, Nebraska
Customer: Environmental Monitoring and Reporting Branch

Introduction and Objectives

High Pressure Liquid Chromatography (HPLC) can separate most elements from their different valence forms in a liquid sample. By using a reversed phase cation exchange resin organo-metallic compounds may also be separated. This technique used in conjunction with Direct Injection Nebulization (DIN), and detection by ICP-MS, will produce sensitive and fast analysis. In general, conventional techniques use a labour intensive and a time consuming extraction procedure before analysis. LC-DIN-ICP-MS eliminates a lengthy sample pre-treatment. Conventional detection techniques include atomic absorption and ICP-AES. ICP-MS detection will provide detection limits one to two orders of magnitude lower.

There is a customer need to have an accurate and precise method for the determination of organo-tin compounds. A feasibility study is now being conducted using LC-DIN-ICP-MS to determine total organic tin. This technique is faster and more sensitive than the conventional method of liquid extraction and detection by gas chromatography atomic absorption.

Another feasibility study is underway for the analysis of hexavalent chrome in industrial waste by LC-DIN-ICP-MS. This technique will again offer a faster and more sensitive method at lower cost.

Results

Results have been shown that total organo-tin compounds can be collected on a micro-disc column and removed quickly by an acidic eluent. Good precision and accuracy has been shown. This technique would act as a screening device for all samples submitted. Samples containing concentrations of a certain threshold would be set aside and put through a reversed-phase cation exchange column to separate out compounds of interest. In addition to organo-tin, we have been able to detect total organo-mercury compounds.

The hexavalent chrome work is proceeding well. Using the LC-DIN-ICP-MS technique, we have characterized the detection system for Cr+3 and Cr+6 aqueous standards. The separation has been optimized for column eluent flowrate, eluent strength, and retention time have been established. Preliminary detection limit capability is approximately 30 ppt.

Work To Be Completed

The micro-column characterization to DIN for organo-tin and mercury is being completed at Cetac Technologies in Nebraska. We will be applying this system to ICP-MS at a later date. Preliminary work involving specific organo-tin compound analysis will be carried out at the Ministry.

The application of the hexavalent chrome technique is now proceeding at the Ministry. Accuracy and precision determinations, spike recovery, automation, and comparison results on the existing technique must yet be carried out. Although the above work is preliminary, we have succeeded in showing the potential benefits of the technique.

III. Methods for Regulation 347 - Waste Derived Fuel

Study Leader: Rusty Moody
Study Team: Ray Leger, George Wood, Ram Sadana, Pamela Wee
Customer: Industrial Hazardous Waste Section

Introduction and Objectives

Regulation 347 has a section dealing with Waste Derived Fuel. This fuel is burned by small units for heating purposes, generally in garages. The prime concern is the effect on the air quality by burning this waste oil. Owners of these heating units must obtain a Certificate of Approval (C of A) before burning a batch of oil. The C of A specifies parameters and concentration levels which cannot be exceeded. LSB analysis requests will come from investigations into the burning of oil which has not passed the C of A. These methods are required for LSB to analyze samples received from abatement and enforcement activities of MOEE.

Results

The required methods are for selected metals, total halogens, nitrogen, phosphorus, sulphur, water, bottom sediments and ash. Completed work on the various methods is summarized below:

Selected Metals. Regulation 347 requires analysis of samples for arsenic, lead, chromium and cadmium. The C of A requirements also list iron, barium, zinc, beryllium, manganese, nickel and silver. A method has been developed for metals (except As) by ICP following ashing. The first draft of the method has been completed. Recoveries for metals using metal salt or organo-metallic spikes have generally exceeded 90% except for copper, titanium and silver. The next steps will be to obtain standards to check the method and to improve the recoveries for the three metals listed above. The method for arsenic involves ignition in a bomb calorimeter followed by analysis by hydride generation. Initial recovery studies gave only 52% recovery. The low recovery may have been due to the nature of the salt used. Future work will involve trying different arsenic compounds and altering the collection solution to increase the recovery of the arsenic.

Total Halogens. This method involves ignition in a bomb calorimeter followed by a potentiometric titration with a silver electrode. Rather than titrate directly with silver, we found that more consistent results were obtained by adding an excess of silver ions and back titrating with chloride. A draft method has been written. Collection of data for recovery and precision criteria is the next step. The titration step can also be used for analysing total halogens in cement following dissolution in nitric acid. Comparison with an external lab for total halogens in cement were within 0.1%, so we have confidence in this portion of the method.

Phosphorus and Sulphur. Pamela Wee of the Emission Spec Unit is helping with this method. An aliquot from the ignition in the bomb calorimeter is analysed using an ICP. Sulphur recoveries have been greater than 85%. No work has yet been done on phosphorus.

Water and Bottom Sediments. A method from the literature (ASTM) will be evaluated. It has the benefit of being straight-forward, and appears to meet our analytical requirements.

Ash. Preliminary work has been done following an ASTM method. No ASTM method yet exists for waste crankcase oil. Other laboratories which must analyse this matrix simply employ standard ash tests.

Nitrogen. Work on this method has not been initiated.

Work to be Completed

Remaining work on this project is summarized in the individual method descriptions above.

IV. Determination of Dimethylamine and Related Compounds in Water

Study Leader: Otto Meresz
Study Team: Marika Hatnay, Barry Ali, Yvonne Jones
Customer: Science and Technology Branch, Plant Optimization

Introduction and Objectives

In 1989, when detectable levels of N-nitrosodimethylamine (NDMA) were found in the treated water supply of Ohsweken, it was suggested that it was formed during the water treatment process - most likely from dimethylamine (DMA). It was necessary to develop an analytical method capable of quantitation of DMA in raw water at concentrations as low as 1.0 microgram per liter (1.0 part-per-billion).

Results

Dimethylamine is a gas at room temperature, and is so soluble in water that it cannot be effectively extracted by using water-immiscible organic solvents. Therefore, an in-situ derivatization reaction with p-Toluenesulphonylchloride was chosen to obtain N,N-Dimethyl-p-Toluene-sulphonamide (DMPTSA), which can be readily extracted from water and determined by using gas chromatography.

A method was developed based on the above derivatization that is capable of detecting DMA in water at concentrations as low as 1.0 ppb. So far, over 60 samples of water from the Grand River have been analyzed for DMA by using this method.

Work to be completed

Results from the initial method development and survey analyses are being prepared for publication. Additional development is needed to investigate other water contaminants which may be precursors to NDMA.

V. New Sample Preparation Method for NDMA

Study Leader:	Steve Jenkins
Study Team:	Vince Taguchi, Dave Wang, J-P. Palmentier, Kim Hong, Pernille Jorgensen
Customer:	Science and Technology Branch, Plant Optimization

Introduction and Objectives

The original sample preparation procedure for N-Nitrosodimethylamine (NDMA) was based on liquid-liquid extraction with dichloromethane and sample clean-up by acid-base partitioning. This was followed by drying and concentration. Sample throughput was limited to 1 procedure blank, 1 spiked control sample and 7 samples per 11-hour day.

An alternative method was investigated to increase the productivity to accommodate increased workload. Other goals were to reduce solvent consumption, reagent use and glassware requirements, to improve the precision, accuracy and detection limit and to reduce the cost. Also, productivity could be maintained with fewer staff.

Results

The new method was based on extraction with a granular adsorbent, Ambersorb 572, in the sample bottle. This was followed by filtration and air-drying. The dry granules were transferred to an autosampler vial. Dichloromethane was added and the vial was capped. Extraction of the NDMA occurs in this vial. Productivity was increased by a factor of 3-4 (3 procedure blanks, 9 spiked control samples and 20 samples per day). The precision, accuracy and detection limit were also improved while the solvent consumption, reagent use and glassware requirements were reduced.

Work to be Completed

The new method was completed and brought on-line in December 1993. A paper describing the method development and validation has been submitted for publication in a scientific journal.

VI. GC/MS Analysis of PAH in Drinking Waters

Study Leader: Patrick Crozier
Study Team: L. Matchuk
Customer: Environmental Monitoring and Reporting Branch

Introduction and Objectives

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. The carcinogenic nature of some PAHs has elicited their inclusion in environmental control legislation. In drinking waters the World Health Organization (WHO) has recommended the maximum permissible concentration for six representative PAHs (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(123-cd)pyrene) not to collectively exceed 200 ng/L. The Ontario Ministry of Environment and Energy has established the maximum acceptable drinking water guideline for benzo(a)pyrene itself to be 10 ng/L.

Currently LSB test protocols for polynuclear aromatic hydrocarbons (PAHs) in drinking/surface waters utilize HPLC/Fluorescence methodology. This method is costly, prone to down-time and uses large quantities of a solvent with known environmental and health hazards (acetonitrile). A PAH analysis method using GC/MSD will provide reliable low level drinking water data with the added bonuses of decreased analysis time, expanded linear range and mass spectrometry confirmation. The benefits of a GC/MSD method are :

- Decreased turn-around times (less down-time / shorter analysis time / fewer sample re-analysis)

- Increased analytical capacity (less wet chemical preparation / shorter instrument analysis time)
- More reliable data (mass spectrometry confirmation / elimination of false positive results / isotope dilution methods possible)
- Hazardous solvent reduction (reduction in acetonitrile usage and solvent recycling costs).

Results

A DWA study, entitled "Evaluation of HP5971E - Benzo(a)pyrene Sensitivity", proved a Beta test site HP5971E GC/MSD system (pre-production equivalent to the HP5972 MSD) to be capable of achieving instrument detection limits low enough to reliably monitor PAHs in drinking waters.

Work to be Completed

Differences in the performance characteristics of the new LSB HP5972 MSD system versus the Beta test site HP5971E MSD system will be documented. New wet chemistry preparation techniques to improve method precision will be investigated.

VII. Disinfection By-Products

Study Leader: B. Berg
Study Team: W. Offenbacher
Customer: Environmental Monitoring and Reporting Branch

Introduction and Objectives

Chlorine is a widely used disinfectant treatment in drinking water treatment plants. Chlorine is highly reactive and combines very quickly with many naturally occurring organic compounds (humic materials) to produce chlorinated organics. The dominant chlorination products are chloroform, trihalomethanes (THMs) and chlorinated

aliphatic acids, especially dichloroacetic acid (DCA) and trichloroacetic acid (TCA). Trihalomethanes represent only a small portion of the total halo-organics produced, with the majority of disinfection by-products being non-volatile polar compounds. It has been estimated that under normal drinking water treatment plant regimes the formation of halo-acetic acids (HAAs) and halo-acetonitriles (HANs) exceeds THM formation by three to five times. Trihalomethanes are routinely determined in drinking water but simple methods for the analysis of ug/L (ppb) concentrations of the non-volatile, highly soluble chlorinated carboxylic acids and acetonitriles do not exist. Determination of halo-acetic acids and halo-acetonitriles in drinking water is important not only from the standpoint of their being present at significant concentrations but also because many of these compounds are suspected or confirmed carcinogens.

Results

Investigations have concentrated on the halo-acetic acids with the halo-acetonitrile work put on hold. Literature searches have been completed. A HAAs GC/ECD instrument analysis method has been developed. The testing of various extraction methods is underway. Solid phase extraction (SPE) techniques (resin cartridges, ion exchange cartridges, etc..) have been tested with only moderate success. SPE methods appear to work well for relatively high (ppb) levels of HAAS but do not produce consistent results at the low ppb and ppt level necessary for drinking water monitoring. Micro-extraction techniques using various extraction solvents are being tested.

Work to be Completed

Evaluation of GC-ECD, GC-MSD and GC-ITD instrumentation for analysis of HAAS and HANs has been completed. All wet chemistry preparation evaluation and method validation must be completed.

VIII. Expansion of Drinking Water Analyses Capabilities

Study Leader: P. Crozier
Study Team: L. Grey
Customer: Environmental Monitoring and Reporting Branch

Introduction and Objectives

The Ontario Ministry of Environment and Energy is currently revising the Ontario Drinking Water Objectives. The new Drinking Water Objectives have been expanded from 18 organic target compounds to 49 semi-volatile pesticides and industrial chemicals. LSB does not have the analytical capability to analyse for 18 of these 49 target chemicals. The following is a listing of the compounds not analysed by the LSB but will appear in the new Drinking Water Objectives :

'Ontario Drinking Water Objectives' Organic Compounds not on LSB Drinking Water Analyses Target Compound Lists		
Aldicarb	Diquat	Terbufos
Azinphos-methyl (guthion)	Glyphosate	2,3,4,6-Tetrachlorophenol
Bendiocarb	Nitrilotriacetic acid (NTA)	Triallate
Bromoxynil	Paraquat	Trifluralin
Diclofop-methyl	Picloram	Dinoseb
Dimethoate	Temephos	2,4-Dichlorophenol

In order to fulfil the MOEE environmental monitoring mandate LSB is endeavouring to develop analytical methods to test for the new organic target compounds.

Results

LSB is concentrating on the addition of those compounds which will fit into existing analytical scans before attempting to develop analytical techniques which will

require the acquisition of new analytical equipment and/or the dedication of staff for single compound analysis methods. The incorporation of bromoxynil, 2,4-dichlorophenol (24-DCP), dinoseb, diclofop-methyl, dimethoate, picloram, 2,3,4,6-tetrachlorophenol (2346-TCP), temephos, terbufos and trifluralin in existing LSB drinking water scans is being investigated.

Organophosphorus Pesticides: Dimethoate, terbufos and azinphos-methyl instrument performance characteristics have been documented. Recovery studies are nearing completion. Method "W" values will be in the 20 to 50 ng/L range. Several minor problems are being addressed before incorporation into the organophosphorus pesticides scan. Temephos can not be added to the organophosphorus scan because it is heat labile but it is detected nicely by HPLC using either the carbamate or phenyl urea analysis conditions.

Chlorinated Pesticides: Trifluralin has been added to the chlorinated organic pesticides/PCBs scan. The "W" value is 5 ng/L and the "T" value is 50 ng/L.

Chlorophenols (CPs) and Phenoxyacid Herbicides (PAs): Instrument conditions and performance characteristics have been established for 24-DCP, 2346-TCP, bromoxynil, dimethoate, dinoseb, diclofop-methyl and picloram. Wet chemistry recovery studies are underway. Plastic SPE cartridges are being evaluated which are suitable for CP/PA analysis and give reasonably consistent recoveries of picloram.

Work to be Completed

Organophosphorus Pesticides: The stability of dimethoate in analytical standards must be investigated. The immediate disappearance of terbufos in chlorinated waters is also being investigated.

Phenoxyacid Herbicides: Recovery data must be gathered for the inclusion of 24-DCP, 2346-TCP, picloram, diclofop-methyl, bromoxynil and dinoseb in the chlorophenol/phenoxyacid herbicides scan.

Methodology Enhancements

Introduction

Much of the method development research performed at the Laboratory Services Branch is in response to customer requests to monitor new environmental contaminants or to expand the scope of specific methods to different sample types. In addition to this research, Laboratory Services Branch staff regularly initiate projects designed to improve services to our customers. Objectives of LSB-generated research commonly include improving the ruggedness of methods, achieving lower detection limits, increasing sample throughput and reducing cost, increasing the degree of automation, reducing the use of toxic solvents, and generally improving the quality of analytical data including precision, accuracy, and freedom from interferences.

Methodology enhancements that address the above considerations are an ongoing activity of any modern analytical laboratory. To remain at or near the analytical state-of-the-art, these activities are essential. A large range of enhancements to methods are possible, from simple adjustments to sample extraction times, to major changes such as the use of a completely different detection system. In this report are listed the major studies. Although generated internally, the results of these projects will result in substantial data quality and turnaround time improvements for Laboratory Services Branch customers.

I. Application of Robotics to Routine Sediment Extraction

Study Leader: Gerald Ladwig
Study Team: Dan Toner
Benefit: Increased Sample Throughput

Introduction and Objectives

The main objectives of this project are:

1. to automate the extraction portion of a manual sediment method
2. to extend the usefulness of existing equipment
3. to improve analytical results and throughput of the method

Results

The current use of robotics in the Biota and Sediments lab involves the extraction of acid digested fish tissue with a Zymate II robotic system. In an effort to more efficiently utilize this equipment, development work was undertaken to attempt to extract sediment samples using the system in its current configuration. After discusions with Zymark Ltd., it was decided to implement a sediment extraction routine using vortex agitation of samples. Method development consisted of evaluation of different solvent systems and required changes in manual procedures to make them amenable to automation.

An analysis method based on use of the robotics system was developed and is being evaluated. Minimum sample throughput required is on the order of 30/day, which the system is capable of achieving quite easily. This system automates only the extraction portion of the method,with samples going through additional Florisil column clean-up and instrumental analysis. To date, the system has been found to be equivalent to or better than the manual method.

Work to be Completed

The development work for the analysis of PCBs, organochlorine pesticides, and chlorobenzenes in sediment and soil samples is complete. Robotic extraction for these parameters has been appended to the method. Statistical comparisons show that PAH recoveries are the same as those obtained from previous work. Method documentation needs to be updated.

II. Microwave Digestion Technique for Trace Metals Analysis of Vegetation, Soil, and Sediment

Study Leader: Liz Pastorek
Study Team: Jane Thrush
Benefit: Faster Sample Turnaround, Laboratory "Greening"

Introduction and Objectives

Historically, the MOEE lab has carried out its vegetation, soil, and sediment metals' sample preparation using a strong mixed acid heated digestion. This tends to be labour intensive, time consuming and potentially unsafe. The latest developments in the sample preparation area have included various microwave techniques. One of these, the high pressure vessel microwave system, while relatively fast is still labour intensive. Flow - through systems are being developed that could save staff time while matching the present methods in extraction capability.

As an initial step a flow - through system, from CEM, was brought in for evaluation.
Primary objectives were to:

- carryout metals' preparation of soil and vegetation matrices to produce results to within +/- 20 % of initial agreement of present method results;
- ensure no carryover or contamination of samples;
- preserve the present detection limits;
- improve throughput time at the preparation stage;

Results

A throughput study showed that the new method resulted in a savings of 40% to 50% of the staff time required for sample preparation. No sample cross-contamination as a result of using the microwave digestion system was observed. Analysis of vegetation samples by using this method compared to conventional sample digestion techniques showed good agreement for most analytes, but comparative testing of soil samples indicated that more than one digestion method may be necessary to obtain acceptable results for all analytes.

Work to be Completed

Other available microwave systems (i.e. Questron) will be evaluated. Once an acceptable instrumental system is chosen, detailed optimization studies must be performed, followed by method validation by parallel testing with the present method.

III. Negative Ion Chemical Ionization (NICI) Confirmation of Halogenated Organics

Study Leader:	Don Robinson
Study Team:	Vince Taguchi, Kim Ngo
Benefit:	Improved Capability to Identify Unknown Organic Compounds

Introduction and Objectives

Confirmations of halogenated organics previously analyzed by GC-ECD and that are present in high concentrations are done by GC/MS in the positive ion electron ionization (EI) mode. Confirmations of halogenated organics previously analyzed by GC-ECD and present in low concentratons cannot be done by GC/MS in the positive ion EI mode.

An alternative ionization technique is NICI. Sensitivity comparable to an ECD can be obtained. In addition to retention time data, mass spectral information that is confirmatory can be obtained.

Results

The Hewlett-Packard MSD's at MOEE do not have the capability to do positive ion chemical ionization (PICI) and NICI. The Finnigan 4500's (1979 and 1981 vintage) were modified with a reagent gas manifold system to do PICI and NICI confirmations. The NICI confirmations are now routine. Because NICI spectra are instrument-dependent and libraries cannot be purchased (the NIST libraries contain EI spectra only), Don Robinson is in the process of creating an NICI library for the Finnigan 4500's. Confirmations of toxaphenes and PCB's have been done in fish extracts for the Thunder Bay laboratory. Additional samples have been included in this year's workload planning.

Work to be Completed

The hardware set-up has been completed. NICI confirmations are routine and have been incorporated into method E3335A "The Confirmation/Identification of Organic Compounds by Gas Chromatography/Mass Spectrometry". This method also includes PICI confirmations and confirmations by GC/(full scan)MS by conventional EI. The creation of the NICI library is on-going.

IV. The Application of Solid-Phase Extraction (SPE) for Sample Preparation in Waste Water Analysis

Study Leader: Rocsana Lega
Benefit: Faster Sample Turnaround, Laboratory "Greening"

Introduction and Objectives

Preparation of waste water samples for instrumental analysis normally involves an enrichment step and a cleanup step. Our traditional existing methodologies, involve liquid -

liquid extraction of pH adjusted water sample with an organic solvent. The organic extract is dried and concentrated to small volumes, prior to fractionation or cleanup over Florisil packed chromatographic columns. Significant progress has been made in analytical instrumentation and data management in the last years but sample preparation has remained virtually unchanged. The existing methodologies, though well established can not be easily automated, are time consuming and laborious, requiring relatively large quantities of potentially toxic solvents. The absorbent material (Florisil) and the solvents are not recycled and the time for the preparation of chromatographic columns and the evaporation of solvents contributes to the overall cost of analysis. Over the last decade, sorbent extraction has proved as a powerful tool for chemical isolation and purification. Similar to low pressure chromatography, it involves the use of small, disposable extraction columns, filled with one of a wide variety of sorbents. Sample cleanup, sample concentration and matrix removal are the three most popular uses of solid phase extraction.

Environmental applications of solid phase extraction for the determination of organic pollutants in water samples have been reported. Methods for the cleanup and concentration of organic contaminants from drinking water are in use, but there is not a technique applicable to different aqueous sample types including industrial effluent. The presence of high concentrations of interfering compounds, turbidity and solid particulates can affect the efficiency of SPE methods. The target compounds for this work are chlorophenols and phenoxy acids.

The objectives of this work are:

1. to assess the feasibility of using SPE technique in wastewater sample preparation,
2. to develop a reliable solid phase extraction methodology that may be adopted as a routine procedure in the waste-water unit, and
3. optimization, automation and validation of the SPE technique using Zymark AutoTrace SPE Workstation.

Results

A solid-phase extraction method was developed for automation by using an Autotrace SPE Workstation. GC/MS (ion trap) conditions for target compound determinations were established. Various experimental conditions such as the choice of elution solvent and drying times were studied. Quality control data such as analyte recoveries and method detection limits were determined for each target compound. The new method was validated by the analysis of spiked real-matrix samples.

Work to be Completed

Development work on the new method is completed.

V. Hexane Micro-Extraction Roller Methodology

Study Leader : P. Crozier
Study Team : I. Albrecht, J. Mazur
Benefit: Faster Sample Turnaround, Increased Sample Capacity, Laboratory "Greening"

Introduction and Objectives

The implementation of micro-extraction methods within the Drinking Water Analyses Section will benefit all Laboratory Service Branch customers. The Laboratory will be able to increase productivity, reduce solvent usage and reduce analytical costs while maintaining analytical quality. In fact, analytical quality and method detection limits will be enhanced by the reduction in sample/extract manipulation associated with micro-extraction technology.

Micro-extraction techniques are being tested and analytical methods developed for implementation within the Drinking Water Analyses Section. The first routine analytical micro-extraction method in the process of being developed covers chlorinated organic pesticides and PCBs. This technique has been successfully applied to several pesticides and PCBs by the U.S. Environmental Protection Agency (USEPA Method 505). The list of compounds covered by USEPA Method 505 is limited and the detection limits are much higher than required by MOEE monitoring programs. Work is centring on the expansion of the analyte list and lowering of method detection limits.

Micro-extraction involves the manipulation of extraction conditions in such a manner that analytes of interest can be extracted from water using a minimum amount of organic solvent. In the newly developed Drinking Water Analyses Section method, target analytes are extracted from water using small amounts of hexane. The hexane extract can then be directly analysed by dual capillary gas chromatography without further need for expensive and labour intensive wet chemical processing.

Micro-extraction techniques offer a significant number of advantages over traditional liquid/liquid extraction techniques presently being used. Solvent usage is reduced by a factor of 100 and other chemicals such as sodium sulphate (drying agent) are virtually eliminated ("Laboratory Greening"). Sample extract manipulation will be reduced significantly. No extract concentration (evaporation), drying or clean-up is required.

Results

The micro-extraction method reduces the time for wet chemical sample preparation by 75% and eliminates the need for large quantities of hazardous chemicals. Dichloromethane usage is virtually eliminated. Distribution curves and equilibrium times have been established for each target analyte. Target analyte recoveries have been tested at spike levels from high pg/L (ppq)

to low ug/L (ppb). Average recoveries of the 37 individual chlorinated organic pesticides, chlorinated organic industrial chemicals and PCBs tested exceeded 80%. Relative standard deviations (RSDs) were in the order of 2-8%.

Work to be Completed

Work on the actual method is complete. The method write-up/bench procedure is in the process of being completed. Method testing on a wide variety of real matrix spikes and validation against the current dichloromethane extraction method is nearly complete. The comparison of the micro-extraction method and current dichloromethane extraction method should give statistical information on any potential differences in analytical results which could be method related. This is very important to Drinking Water Analyses Section customers who have large databases of LSB data which is continually used for environmental trend analysis.

Publications and Presentations

1. P. Crozier, W. Offenbacher, W. Berg, and D. Hall. *The Application of Micro-Extraction Roller Methodology to Trace Level Pesticides Analyses of Drinking Water*, presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.

VI. Extraction Methods for Dioxins/Furans in Aqueous Samples

Study Leader:	Kathy Taylor
Study Team:	Dave Waddell, Karen MacPherson, Eric Reiner
Benefit:	Faster Turnaround, Laboratory "Greening"

Introduction and Objectives

In the LSB standard methods, Dioxins/Furans are extracted from aqueous water samples by liquid/liquid extraction using pentane (drinking water) or methylene chloride (other aqueous samples). This extraction method is slow, laborious, and requires the use of large quantities of solvents. Recent developments in solid-phase extraction offer the possibility of performing such extractions by passing water samples through a solid phase extraction membrane. In this study, the use of Empore disks for extraction of dioxins/furans from aqueous samples is investigated. Extraction methods based on Empore disks are expected to be simpler and quicker than the existing liquid-liquid extraction procedure, and should reduce the use of solvents. In addition, the use of dichloromethane for extractions can be eliminated.

Results

Our earlier work showed that the extraction of dioxins/furans from aqueous samples by using Empore disks was highly efficient. Recent studies focused on methods for efficient recovery of the dioxins/furans from the Empore disks. Soxhlet extraction of the Empore disk was replaced by direct elution by using small quantities of an ethanol/toluene mixture (70:30). Samples did not require filtration prior to Empore disk extraction, but different filter media were used in combination with Empore to optimize sample flow through the disk.

Over 35 industrial effluent samples and 14 spiked matrix samples have been analyzed to test the new method. No differences were found in dioxin/furan recoveries obtained by using direct solvent elution compared to Soxhlet extraction.

Work to be Completed

Empore disks are available in two standard sizes, 47mm diameter and 90 mm diameter. The extraction method works well when 90 mm disks are employed, but extractions are very slow when 47 mm disks are used. Work to improve the extraction time with 47 mm disks, especially when particulates are present, is ongoing. Additional samples will be analyzed to determine the analytical figures of merit for this procedure.

Publications and Presentations

1. E. Reiner, K. Taylor, and L. Grey. *Determination of PCDDs and PCDFs in Various Waters*, presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.

VII. Solid-Phase Extraction Cartridges for Dioxin/Furan Cleanup

Study Leader: Kathy Taylor
Benefit: Faster Turnaround, Lower Test Cost, Laboratory "Greening"

Introduction and Objectives

The determination of dioxins/furans in a wide variety of sample types is one of the most expensive, lengthy, and difficult procedures in trace environmental analysis. Considerable cost and time savings for dioxin/furan determinations could be realized by simplifying the sample cleanup procedures which can take three or more working days to perform. In this project, the use of solid-phase extraction (SPE) cartridges for cleanup of dioxin/furan sample extracts is

investigated. Benefits of SPE-based cleanup methods could include more rapid sample analysis, reduced solvent use, lower per sample cost, and improved analytical reproducibility.

Results

Initially, an SPE-based procedure reported in the literature by Chang et al was examined. This method was a dual-column cleanup procedure based on use of cation exchange column and a silica column. A final florisil-cartridge cleanup was also employed. The literature method was found to give excellent recoveries of PCDDs/PCDFs spiked onto soil samples. However, cleanup efficiencies were not adequate for extracts of 5-gram samples from soil samples known to contain high concentrations of Polycyclic Aromatic Hydrocarbons and Chlorinated Diphenyl Ethers.

Work to be Completed

Modifications of the literature procedure to accomodate samples with high concentrations of potential dioxin/furan interferences are underway. The possibility of collaborative work with the National Research Council is being investigated.

VIII. LC/MS Analysis of Environmental Samples

Study Leader:	Carolyn Koester
Study Team:	Vince Taguchi, J-P. Palmentier, Dave Wang, Kim Ngo and Pernille Jorgensen
Benefit:	Expanded Capability to Detect Polar and High Molecular Weight Organic Compounds

Introduction and Objectives

There are several LC/MS techniques that are available: thermospray, particle beam, electrospray, IonSpray, continuous-flow FAB. Particle beam LC/MS was selected because EI and CI mass spectra can be obtained. The EI spectra can be searched through the same NIST libraries that are on the GC/MS systems. The goals were two-fold:

(a) -to analyze target compounds not amenable to GC analysis (i.e. thermally-labile, polar, etc.)

(b) -to do organic characterization by LC/MS to complement GC/MS analyses

Results

Carolyn Koester was the PDF assigned to be the principal investigator. The first year of the PDF was spent solving hardware problems. Three nebulizer designs were evaluated. The first two gave irreproducible results. The third design gave reasonable performance but was subseqently modified to optimize the system.

For the target compound analyses, thermally-labile pesticide/herbicides were analyzed by LC/MS. These included carbaryl, carbofuran, diuron, linuron, siduron and rotenone. Ppb detection limits were obtained by full scan. Low ppb detection limits are expected by selected ion monitoring (SIM). However, the calibration curves were non-linear. This non-linearity is affected by the organic content of the sample extract which affects the transport efficiency across the interface. There are two possible solutions to the quantitation problem. The first is quantitation by diode array UV detection and confirmation by MS. The other is isotope dilution LC/MS. The latter option would require isotopically-labelled analogues for all of the target compounds.

N-nitrosodiphenylamine (NDPhA) and diphenylamine (DPhA) cannot be differentiated by GC/MS because NDPhA decomposes to DPhA in the GC. However, they can be analyzed by LC/MS because the chromatography is carried out at ambient temperature. NDPhA and NPhA are separated by reverse phase LC and confirmed by mass spectrometry.

Characterization of extracts previously analyzed by GC/MS were analyzed by reverse phase LC/MS. Unlike GC/MS, a single LC column cannot accommodate a broad range of organics. While some components have been identified by reverse phase LC/MS, there has been limited success for general organic characterization. This is partly due to the chromatographic limitations of HPLC.

Work to be Completed

The quantitation of the pesticides/herbicides will be developed with the diode array detector. The availability of isotopically-labelled analogues will be investigated. A suitable sample preparation scheme will be developed. An isotope dilution method for NDPhA and NPhA will be developed. The d_{10}-labelled analogues have been purchased. A normal phase LC/MS system will be set up and evaluated for organic characterization. The extracts previously run by GC/MS and reverse phase LC/MS will be run by normal phase LC/MS. Fractionation of the extracts may be necessary.

Publications and Presentations - 1993 Laboratory Services Branch

A. Publications

1. B. Jobb; R.B. Hunsinger; V.Y. Taguchi; O. Meresz. *Removal of N-nitrosodimethylamine (NDMA) from the Ohsweken (Six Nations) Water Supply: Interim Report July 1993.* Ontario Ministry of Environment and Energy Report (ISBN 0-77781-542-7), **1993.**

2. J. McBride; P. Campbell. *Stability Study, 4-AAP Phenolics in Preserved Samples.* Ontario Ministry of Environment and Energy, Laboratory Services Branch Report (ISBN 0-77780-685-1), **1993.**

3. B. Jobb; R.B. Hunsinger; O. Meresz; V.Y. Taguchi. *A Study of the Occurrence and Inhibition of Formation of N-nitrosodimethylamine (NDMA) in the Ohsweken Water Supply.* Proceedings of the 1992 Water Quality Technology Conference, American Water Works Association, **1993**, pp 103-131.

4. C. Chan; R. Sadana. *Automated Determination of Mercury at Ultra Trace Levels in Waters by Gold Amalgam Preconcentration and Cold Vapour Atomic Fluorescence Spectrometry.* Analytica Chimica Acta **1993**, *282*, 109-115.

5. C.J. Koester; R.E. Clement. *Analysis of Drinking Water for Trace Organics.* CRC Critical Reviews in Analytical Chemistry **1993**, *24*, 263-316.

6. R.E. Clement. *The Ontario Ministry of the Environment Dioxin Laboratory.* Proceedings of the 1992 Water Quality Technology Conference, American Water Works Association, **1993**, pp 2023-28.

7. R.E. Clement; G.A. Eiceman; C.J. Koester. *Environmental Analysis.* Analytical Chemistry **1993**, *65*, 85R-116R.

8. S. Cussion; D.E. King; S.S. Selliah. *Phenolics (4-AAP) in Reagent Water and Surface Water.* Ontario Ministry of Environment & Energy, Laboratory Services Branch Report (ISBN 0-77780-591-X), 1993.

B. Presentations

1. R.E. Clement and C.J. Koester, *Laboratory Careers in the Environment*, Lecture Presented to High School Students of West Humber Collegiate, Toronto, May 13, 1993.

2. R.E. Clement, *Lecturer*, Chem 322: Environmental Analytical Chemistry, Chemistry Department, The University of Western Ontario, London Ontario, September - December, 1993.

3. R.E. Clement, *Dioxins in the Environment*, Lecture Presented to Graduate Students, Environmental Science 501, The University of Western Ontario, November 4, 1993.

4. *R.E. Clement*, "Environmental Laboratories: Service vs Economics"; Invited Talk presented at the Seminar *Ethics, Environment and Business Training for Chemists & Chemical Engineers*, Association of the Chemical Profession of Ontario, York University, November 20, 1993.

5. *R.E. Clement* and C.J. Koester, "State-of-the-Art Methods for Trace Organics in Drinking Water", Invited Plenary Talk presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment: Current Status and Future Directions, October 28, 1993, Burlington, Ontario.

6. *R.E. Clement*, "Dioxins in the Environment: Facts, Myths, and Chemophobia", presented at the University of Michigan, Department of Civil and Environmental Engineering Seminar Series, October 19, 1993.

7. *R.E. Clement*, "The Importance of Chromatography in Trace Dioxin Determination: *The Critical Link in a Fragile Chain*", invited talk presented at the 24th Ohio Valley Chromatography Symposium, Hueston Woods State Park, June 24, 1993.

8. *R.E. Clement*, "Toxic Compounds, Risk, and the Vanishing Zero", invited seminar presented at McMaster University, Department of Chemistry, April 1, 1993.

9. E. Reiner, *K. Taylor*, and L. Grey, "Determination of PCDDs and PCDFs in Various Waters", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.

10. *P. Crozier*, W. Offenbacher, W. Berg, and D. Hall, "The Application of Micro-Extraction Roller Methodology to Trace Level Pesticides Analyses of Drinking Water", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.

11. *B. Jobb*, R Hunsinger, O. Meresz, and V. Taguchi, "N-Nitrosodimethylamine in a Drinking Water Supply", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.

12. *D. King*, "Establishing the Credibility of Environmental Laboratories", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 29, 1993.

13. *C.J. Koester* and R.E. March, "Analysis of Organic Compounds by Liquid Chromatography/Mass Spectrometry", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 29, 1993.

14. V.Y. Taguchi, *D. Robinson*, C.J. Koester, and P. Crozier, "Application of Chemical Ionization (CI) Mass Spectrometry to Environmental Samples", presented at the International Symposium on Chemistry and Biology of Municipal Water Treatment, Burlington, Ontario, October 28, 1993.